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A 3-year continuous record of nitrogen trace gas fluxes from untreated and limed soil of a N-saturated spruce and beech forest ecosystem in Germany

2. NO and NO_2 fluxes

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Abstract. For 3 years we followed the complete annual cycles of NO and NO_2 flux rates from soil of a spruce control site, a limed spruce site, and a beech site at the Höglwald Forest, Bavaria, Germany, with high temporal resolution in order to gain detailed information about (1) the impacts of forest type, liming, and atmospheric N input by wet deposition on the magnitude of NO and NO_2 flux rates and (2) the microbial processes involved in NO production and emission. In addition to identification of seasonal variations of flux rates the huge database allowed calculation of annual mean NO and NO_2 fluxes with high accuracy and identification of interannual variations of fluxes. The long-term annual mean NO_x emission was 61.7 μg NO_x N m^{-2} h^{-1} for the spruce control site, 17.3 μg NO_x N m^{-2} h^{-1} for the limed spruce site, and 4.0 μg NO_x N m^{-2} h^{-1} for the beech site. These extremely high soil NO_x emissions from a temperate forest most likely reflect the status of N saturation of the Höglwald Forest as a consequence of year-long heavy atmospheric N input. Multiple regression analyses revealed the following sequence of importance of environmental factors on NO flux: soil temperature to water-filled pore space to soil NO_3^- concentrations to soil NH_4^+ concentrations. Nitrification was the dominating biotic modulator of NO emission at all sites: >60% of the variation of NO emission rates were associated with variations of net nitrification rates. There was a strong positive correlation between amount of in situ N input by wet deposition and magnitude of in situ NO flux rates. Approximately 15% and 7% of the actual N input was lost as NO from the soil stocked with spruce and beech, respectively. Liming resulted in 49% reduction of NO emissions as compared to an unlimed spruce control site. The results indicate that the reduction in NO emission was due to an increase in NO consumption within the limed soil. In contrast to NO flux, NO_2 flux was modulated by physico-chemical rather than biological factors. Using the data of this study, we estimate that the contribution of N-affected temperate coniferous and deciduous forests to the global NO_x release is 0.3 Tg NO_x N yr^{-1}.

1. Introduction

The nitrogen oxides NO and NO_2 (NO_x, the sum of NO + NO_2) play a central role in both stratospheric as well as tropospheric chemistry. In the stratosphere, NO is produced mainly by the photooxidation of N_2O and is involved with its oxidation product NO_2 in a series of catalytic reactions, which finally result in the destruction of stratospheric ozone (O_3) [*Crutzen*, 1979]. In the troposphere, NO_x is involved together with volatile organic compounds in a sequence of photochemical reactions, which can lead to net tropospheric O_3 production [*Crutzen*, 1970, 1979, 1995]. Tropospheric O_3 is not only of concern as a greenhouse gas but also because of its effects on vegetation, human health, and materials [*Tillon*, 1989; *Guderian et al.*, 1985; *Chameides et al.*, 1994; *Lee et al.*, 1996]. Moreover, there is also growing concern about the consequences of increasing deposition rates of nitrogen oxides on a global scale [*Galloway et al.*, 1994], which contribute to the increasing acidification of soils and N saturation of natural ecosystems, like forests, which in earlier times were typically characterized by N limitation [e.g., *Fenn et al.*, 1996; *Aber et al.*, 1989]. In view of these impacts of NO_x on atmospheric chemistry and the environment it is of vital importance to know the global sources of NO_x. Emissions of NO and NO_2 into the atmosphere are the result of both anthropogenic activities and natural processes. On a global scale, major identified sources of NO_x are fossil fuel combustion, biomass burning, lightning, and microbial emissions from soils [*Lee et al.*, 1997]. Model estimations of global NO_x emissions [*Lee et al.*, 1997] suggest that the global source strength of soils, which had been estimated before to be in the same order of magnitude [*Houghton et al.*, 1990] as fossil fuel combustion (~20 Tg NO_x N yr^{-1}), may have been overestimated in the past. According to model estimations of *Lee et al.* [1997], soils contribute only ~15% (7 Tg NO_x N yr^{-1}) to the global source strength of NO_x (44 Tg NO_x N yr^{-1}). This reduction in the estimate of the global contribution of soils was mainly due to the implementation of a canopy reduction factor, which accounts for in-canopy deposition of NO_x emitted from soils of forest ecosystems. However, a recently published global inventory of NO emissions

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Table 1. Mean, Minimum, and Maximum NO Emission/NO_2 Deposition Rates at the Different Höglwald Forest Sites 1 week Before and 1 week After Chambers (Five per Site) Were Moved by 1–2 m

	Experimental Site	Before Moving of Chambers			After Moving of Chambers		
		Mean	Minimum	Maximum	Mean	Minimum	Maximum
		NO Emission Rate, μg N m^{-2} h^{-1}					
1994	spruce, control	120.0 ± 9.0	106.9	133.3	114.0 ± 20.7	82.9	135.6
	spruce, limed	71.9 ± 5.7	62.8	78.4	59.9 ± 9.0	48.0	70.5
1995	spruce, control	114.3 ± 11.7	94.8	126.4	104.9 ± 5.0	100.1	114.7
	spruce, limed	47.0 ± 7.0	39.6	59.2	44.0 ± 4.4	37.5	49.6
	beech	34.0 ± 4.6	26.0	38.2	26.7 ± 2.4	18.3	35.5
1996	spruce, control	95.0 ± 4.9	89.6	100.7	86.2 ± 23.2	66.0	116.6
	spruce, limed	44.2 ± 2.5	40.5	47.3	36.3 ± 9.7	29.7	50.7
	beech	12.6 ± 4.5	7.5	19.2	11.8 ± 1.8	9.7	13.2
		NO_2 Deposition Rate, μg N m^{-2} h^{-1}					
1994	spruce, control	−24.1 ± 4.2	−30.0	−18.3	−24.1 ± 5.5	−30.6	−17.2
	spruce, limed	−29.9 ± 7.1	−39.7	−21.1	−22.8 ± 5.9	−29.5	−16.0
1995	spruce, control	−36.2 ± 6.6	−45.3	−24.3	−27.6 ± 4.1	−33.4	−21.8
	spruce, limed	−24.5 ± 6.9	−34.1	−13.8	−22.2 ± 2.9	−26.8	−18.5
	beech	−19.7 ± 5.5	−25.9	−10.6	−19.2 ± 3.2	−23.2	−15.1
1996	spruce, control	−15.9 ± 2.7	−20.0	−12.0	−15.9 ± 5.4	−23.0	−11.5
	spruce, limed	−18.4 ± 3.5	−23.6	−14.9	−17.8 ± 5.3	−24.1	−11.1
	beech	−14.3 ± 5.5	−23.1	−6.8	−18.0 ± 7.2	−24.6	−10.3

Mean NO emission/NO_2 deposition rates before and after moving the chambers were not significantly different.

from soils [*Davidson and Kingerlee*, 1997] based on biome stratifications indicates that the global soil NO source strength is ~21 Tg NO N yr^{-1} and thus has an importance similar to that of fossil fuel combustion.

With the exception of the estimate given by *Davidson and Kingerlee* [1997], the estimates of *Lee et al.* [1997] and *Potter et al.* [1996] do not consider the impact of increasing atmospheric N deposition on NO_x flux rates from soils of natural ecosystems. Especially, estimations of the contribution of N-affected temperate coniferous and deciduous forests (the global area of which was estimated to be 10^6 km^2 [*Davidson and Kingerlee*, 1997]) to the global source strength of NO_x are based on a limited number of field measurements, which in most cases were short term, did not cover complete annual cycles of NO and NO_2 flux rates, and thus were subject to a high degree of uncertainty.

Therefore the main objectives of the present study were (1) to follow over several years the complete annual cycles of NO and NO_2 flux rates from soil of a N-saturated temperate coniferous and deciduous forest ecosystem with high temporal resolution in order to identify seasonal and interannual variations in fluxes and to quantify annual NO and NO_2 losses from the forest soils with high degree of accuracy, (2) to identify the impact of forest type and of countermeasures against increasing soil acidity as liming on NO and NO_2 flux rates, (3) to clarify if a direct relationship between the amount of in situ N input from the atmosphere and the magnitude of in situ NO and NO_2 flux rates can be demonstrated and to quantify the amount of N lost from the actual N input in form of NO N, (4) to identify the importance of biotic and abiotic parameters as modulators of NO and NO_2 flux rates from forest soil, and (5) to estimate the contribution of N-affected temperate coniferous and deciduous forest soils to the global NO_x budget.

2. Methods

2.1. Experimental Site and Experimental Design

Details about the experimental site, the Höglwald Forest, are given by *Göttlein and Kreutzer* [1991], *Kreutzer* [1995], and *Papen and Butterbach-Bahl* [this issue]. The studies described here were performed in a 89-year-old Norway spruce (*Picea abies* L. Karst.) and 96-year-old beech (*Fagus sylvatica*) plantation of the Höglwald Forest. Complete annual cycles of NO and NO_2 flux rates were followed since late 1993 at the spruce sites and since September 15, 1994, at the beech site by fully automated measuring systems installed in trailers at each of three experimental sites: spruce control site (untreated), limed spruce site, beech control site (untreated) [see *Papen and Butterbach-Bahl*, this issue]. Since spruce and beech at the Höglwald Forest stock on identical soil type and are exposed to comparable climatic and edaphic conditions [see *Papen and Butterbach-Bahl*, this issue, Tables 1 and 2], the experimental design allows collection of information concerning the effect of forest type (spruce and beech) on NO and NO_2 flux rates. The impact of liming on NO and NO_2 flux rates was studied by comparison of flux rates obtained from soils of the untreated control spruce site and of a spruce site that was limed in March 1994 by surface application of dolomite (4 t ha^{-1}). Additional information about soil characteristics and changes in pH values after liming is given by *Papen and Butterbach-Bahl* [this issue].

2.2. All Year-Round Continuous Measurements of NO and NO_2 Flux Rates

The fully automated measuring system for determination of NO and NO_2 flux rates has been described in detail by *Butterbach-Bahl et al.* [1997]. At each site, five dynamic measuring chambers and one dynamic reference chamber were installed. Each year in September the dynamic chambers were moved by ~1–2 m, which had no significant effect on mean NO and NO_2 flux rates from each site (Table 1).

Therefore five chambers per site were sufficient to account for spatial variability of flux rates. The basic design and the dimensions of the chambers were identical as described for the static chambers used for N_2O flux rate measurements [see *Papen and Butterbach-Bahl*, this issue] with the following adaptations to the requirements of dynamic chamber measurements: the inlet pane for ambient air was located opposite to the outlet pane of the dynamic chambers and possessed nine holes (2.0 cm in diameter), thus avoiding pressure differences between the inlet and the outlet of the measuring chambers during sampling [*Slemr and Seiler*, 1984, 1991]. The only difference between the measuring chambers and the reference chambers was that the reference chamber had an additional Plexiglas pane; that is, it was closed to the forest floor onto which it was placed.

Determination of NO, NO_2, and O_3 concentrations in ambient air and at the outlet of the chambers and calculation of NO and NO_2 flux rates were described in detail by *Butterbach-Bahl et al.* [1997]. At each site a highly sensitive NO_x analyzer (chemoluminescence detector CLD 770 AL ppt plus photolysis converter PLC 760, Ecophysics AG, Dürnten, Switzerland) was used for NO and NO_2 detection. Ozone concentrations in sample air were measured continuously by a TE 49 C (Thermo-Environmental Instruments Inc., Franklin, Massachusetts) in order to correct the measured NO and NO_2 concentrations for O_3 prior to the calculation of NO and NO_2 flux rates [*Butterbach-Bahl et al.*, 1997; *Beier and Schneewind*, 1991; *Remde et al.*, 1993]. Calibration of the NO_x analyzers was performed weekly using 10 ppb NO in synthetic air produced by dilution of recalibrated standard gas (0.997 ppm NO in N_2, Messer Griesheim, Olching, Germany, recalibrated according to standards used within the Tropospheric Ozone Research project (TOR) by the Fraunhofer Institute for Atmospheric Environmental Research (IFU) calibration laboratory) with synthetic air (80% N_2, 20% O_2) using a computerized multigas calibrator (Environics 100, Environics Inc., Tolland, Connecticut). Efficiency of photolytic cleavage of NO_2 into NO was determined as described by *Butterbach-Bahl et al.* [1997]. The detection limit of NO, NO_2, and O_3 was 50, 100, and 100 pptv, respectively, resulting in a minimum detection limit for NO and NO_2 flux rates of 1.0 and 1.5 $\mu g\ NO_2\ N\ m^{-2}\ h^{-1}$, respectively. Positive values of flux rates given in figures and tables indicate net emission rates of NO and NO_2 from the soil into the atmosphere, whereas negative values of flux rates indicate net deposition of NO and NO_2 onto the soil.

2.3. Determination of Microbial Processes

In situ net ammonification, in situ net nitrification, and potential denitrification rates were determined monthly in soil samples taken from the organic layer of the different sites. Soil samples for determination of net ammonification and net nitrification rates were incubated in the laboratory in glass vessels under aerobic conditions at soil temperatures measured in the field. Net ammonification and net nitrification rates were calculated from the difference of NH_4^+ and NO_3^- concentrations at the start and the end of the incubations (96 hours).

Determination of NH_4^+ concentration was performed as described by *Papen and Butterbach-Bahl* [this issue], whereas for the determination of NO_3^- concentrations in the soil samples a more sensitive method was used. This method was first described by *Lensi et al.* [1985] and was modified for determination of in situ net nitrification rates by *Gasche* [1998]. This method is based on the quantitative conversion of NO_3^- N into N_2O N under strictly anaerobic conditions in the presence of 10% acetylene using the soil-endogenic denitrifier population. The N_2O produced (end point concentration) is detected by a gas chromatograph equipped with a ^{63}Ni electron capture detector as described by *Papen and Butterbach-Bahl* [this issue]. In addition to determination of small amounts of NO_3^- within the soil, this method can be used to calculate potential denitrification rates of the soils, provided that the soil samples are directly incubated under strictly anaerobic conditions in the presence of 10% acetylene. From the kinetics of N_2O accumulation within the incubation vessels the potential denitrification rates can be calculated.

Experiments for determination of the contribution of nitrification and denitrification to NO emission were performed on intact soil cores taken from the soils of the different experimental sites. The methodology was described in detail by *Papen et al.* [1993].

2.4. Determination of Apparent NO Compensation Concentrations of Soils

For the determination of apparent [*Conrad*, 1994] compensation concentrations for NO of the soils, the in situ NO flux rates (Y axis) obtained for five individual measuring chambers at each site were plotted against the simultaneously measured in situ NO mixing ratio (X axis) in the sample air at the outlet of the measuring chambers [*Slemr and Seiler*, 1984, 1991; *Conrad*, 1994]. The apparent NO compensation concentration, which is defined as the NO mixing ratio, at which the net NO flux between the soil and the atmosphere is zero [e.g., *Remde et al.*, 1989; *Slemr and Seiler*, 1984, 1991; *Conrad*, 1994], is given by the intercept of the regression line with the X axis. From the intercept of the regression line with the Y axis the gross NO production can be calculated, whereas the slope of the curve represents the NO uptake rate constant (k) [*Remde et al.*, 1989; *Conrad*, 1994].

2.5. Determination of Additional Parameters and Statistical Analyses of Data

Determination of the percent of water-filled pore space (%WFPS) and NH_4^+ and NO_3^- concentrations in the organic layer of the soils as well as statistical analyses were performed as described by *Papen and Butterbach-Bahl* [this issue].

3. Results

3.1. Seasonal Variations of NO and NO_2 Flux Rates at the Different Sites

In Figures 1–4 the annual cycles of daily mean NO and NO_2 flux rates and the fluctuations of air temperature as well as soil temperature in the organic layer of the spruce control site, the limed spruce site, and the beech site are given for 1994–1996. Annual cycles of NO flux rates at all sites showed a strong seasonal pattern, mainly following the annual courses of air and soil temperatures (Figures 1 and 3), i.e., relative low flux rates during winter, increasing flux rates with increasing temperatures until late summer, and thereafter, again decreasing flux rates with decreasing temperatures until late autumn. A seasonal change in magnitude of flux rates was also obvious for NO_2 but was less pronounced (Figures 2 and 4). Though the seasonal pattern of NO and NO_2 emission rates broadly followed the seasonal trend of air and soil temperature, it is obvious that the high dynamics of NO emission rates (especially at the spruce control site) at smaller timescales cannot be exclusively explained by the dynamics of soil and air temperature alone. At certain time periods, other factors, such as precipitation amount or amount of N input by wet deposition, were stronger modulators of NO and NO_2 fluxes than temperature: For example, heavy precipitation events in the beginning of June 1995 [see *Papen and Butterbach-Bahl*, this issue, Figure 1] did lead to a dramatic decrease of NO emission and NO_2

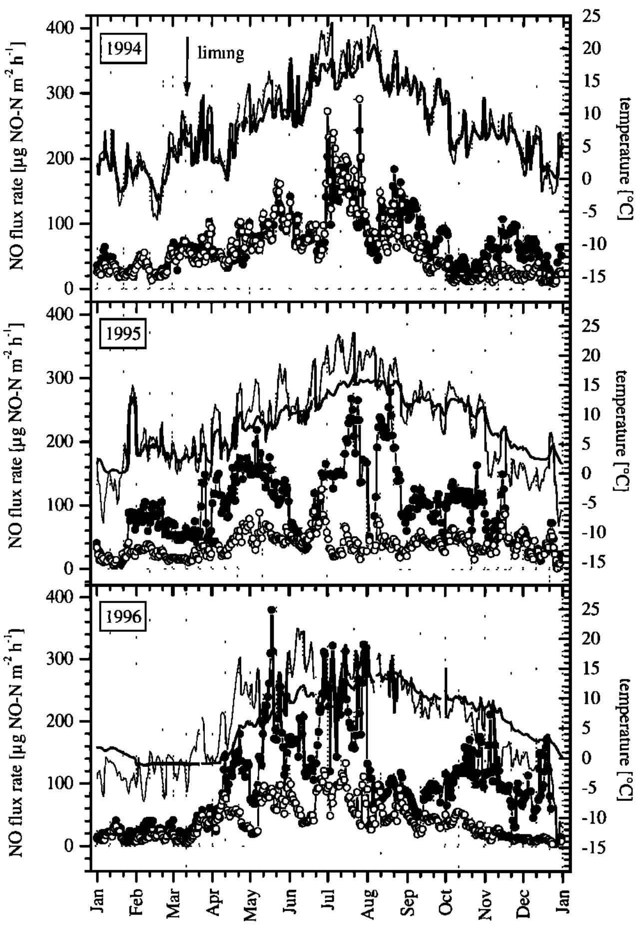

Figure 1. Annual cycles (1994, 1995, 1996) of NO flux rates from the soil of the spruce control site (solid circles) and the limed spruce site (open circles) at the Höglwald Forest and daily means of air (light curve) and soil temperature (organic layer) (heavy curve). Each data point represents the daily mean of NO flux rates from 120 individual flux rates obtained per day from five dynamic chambers installed at each site. Liming (arrow) of the soil (4 t dolomite ha^{-1}) was performed on March 10, 1994.

deposition rates at both the spruce control and beech site despite increasing temperatures (Figures 1–4); the huge temporal fluctuations of increasing/decreasing NO emission and NO_2 deposition rates occurring in May 1996 were more closely related to the extreme amount of N input by wet deposition (highest value observed during the entire observation period: 435 mg N m^{-2} [*Huber*, 1997]) than to total amount of precipitation.

It is clear from the comparison of the time course of NO emission rates at the spruce control and limed spruce site that before application of lime (March 10, 1994), there was no visible significant difference in NO flux rates between both sites. Statistical analysis revealed, indeed, that during this time period there were no significant differences in daily mean NO emission rates at both sites ($p > 0.05$). However, for September 1994 it was found for the first time that the limed spruce site showed significantly ($p < 0.001$) lower NO emission rates than the untreated spruce control site (Figure 1). Thereafter, NO emission rates of the limed spruce site were, with exception of winter months, generally significantly lower than rates at the control site (Figure 1). In contrast to NO fluxes, no significant seasonal differences in magnitude of NO_2 fluxes after liming were detected until the end of the observation period (December 1996) (Figure 2).

A comparison of Figures 1 and 3 shows that for all years of observation the magnitude of NO emission rates from soil of the spruce control site was dramatically higher than those at the beech site, though climatic and edaphic conditions are identical for both forest types at the Höglwald Forest. This pronounced difference between the spruce and beech sites did not apply for NO_2 flux rates.

3.2. Mean Annual NO, NO_2, and Net NO_x Flux Rates and Impact of Liming and Forest Type

The continuous measurements of NO and NO_2 flux rates performed at high temporal resolution allowed us to calculate annual means of NO and NO_2 flux rates with high accuracy for each site and thus to identify interannual variations in flux rates as well as differences in flux rates induced by liming and by forest type (spruce/beech) (Table 2). The mean annual NO emission rate in 1994 at the spruce control site was 72.7 ± 2.1 μg NO N m^{-2} h^{-1} (6.4 ± 0.2 kg NO N ha^{-1} yr^{-1}), i.e., ~1.4 times ($p < 0.001$) lower than the mean annual NO emission rates in 1995 (99.8 ± 3.1 μg NO N m^{-2} h^{-1} corresponding to

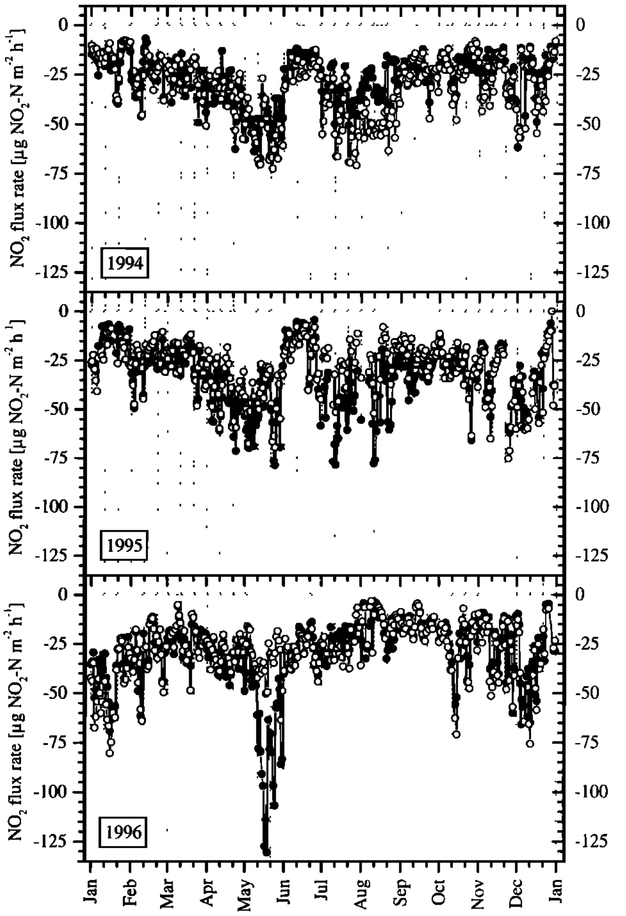

Figure 2. Annual cycles (1994, 1995, 1996) of NO_2 flux rates from the soil of the spruce control site (solid circles) and the limed spruce site (open circles) at the Höglwald Forest. Each data point represents the daily mean of NO_2 flux rates from 120 individual flux rates obtained per day from five dynamic chambers installed at each site.

8.7 ± 0.3 kg NO N ha^{-1} yr^{-1}) and in 1996 (103.5 ± 4.0 μg NO N m^{-2} h^{-1} corresponding to 9.1 ± 0.4 kg NO N ha^{-1} yr^{-1}). The mean annual NO emission rate from the soil of the spruce control site for the entire observation period 1994–1996 (Table 2) was 91.8 ± 1.9 μg NO N m^{-2} h^{-1} (8.0 ± 0.2 kg NO N ha^{-1} yr^{-1}).

The mean annual NO emission rate at the limed spruce site in 1994 was 62.1 ± 2.6 μg NO N m^{-2} h^{-1} (5.4 kg NO N ha^{-1} yr^{-1}) and therefore ~1.6 times higher ($p < 0.001$) compared to annual means calculated for 1995 and 1996 (38.7 ± 1.0 μg NO N m^{-2} h^{-1} corresponding to 3.4 ± 0.09 kg NO N ha^{-1} yr^{-1} and 40.3 ± 1.5 μg NO N m^{-2} h^{-1} corresponding to 3.5 ± 0.1 kg NO N ha^{-1} yr^{-1} respectively). The mean annual NO emission rate from the soil of the limed spruce site for the entire observation period 1994–1996 was 47.2 ± 1.1 μg NO N m^{-2} h^{-1} (4.1 ± 0.1 kg NO N ha^{-1} yr^{-1}). Thus, integrated over the entire observation period 1994–1996, liming led to a highly significant ($p < 0.001$) reduction of the annual mean NO emission rate by ~49% as compared to the spruce control site (Table 2).

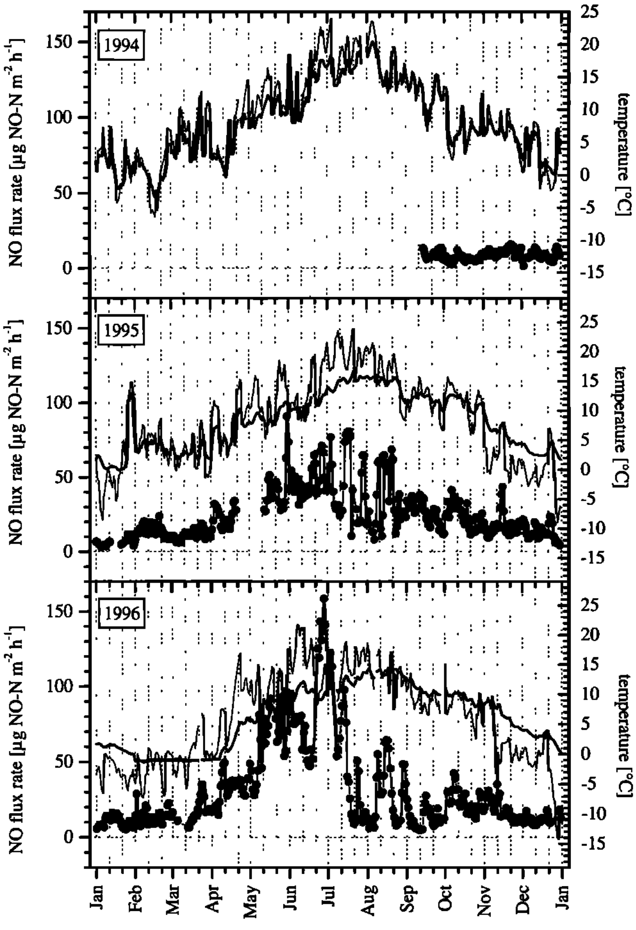

Figure 3. Annual cycles (1994, 1995, 1996) of NO flux rates from the soil of the beech site (solid circles) at the Höglwald Forest and daily means of air (light curve) and soil temperature (organic layer) (heavy curve). Continuous measurements at the beech site started on September 15, 1994. Each data point represents the daily mean of NO flux rates from 120 individual flux rates obtained per day from five dynamic chambers installed at the site.

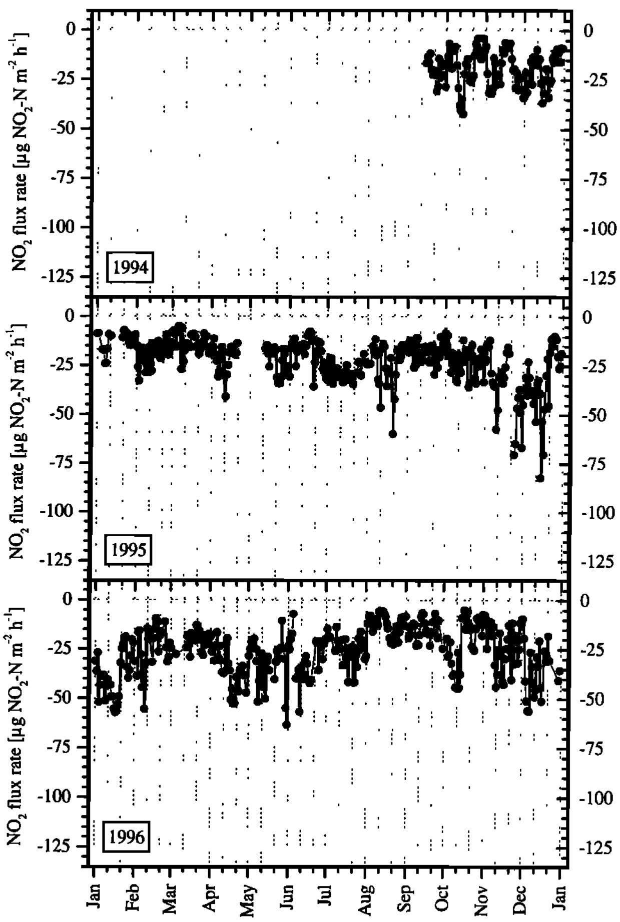

Figure 4. Annual cycles (1995, 1996) of NO_2 flux rates from the soil of the beech site (solid circles) at the Höglwald Forest. Continuous measurements at the beech site started on September 15, 1994. Each data point represents the daily mean of NO_2 flux rates from 120 individual flux rates obtained per day from five dynamic chambers installed at the site.

For the beech site, complete annual cycles of NO and NO_2 flux rates were obtained only for 1995 and 1996 (Table 2). As for the spruce control and limed spruce site (Table 2), there were no pronounced differences in the magnitude of the annual mean NO emission rates between 1995 and 1996, though statistical analysis revealed that the mean annual NO emission rates obtained for 1995 and 1996 were significantly different at all sites ($p < 0.001$). The mean annual NO emission rates at the beech site calculated for 1995 and 1996 were 25.8 ± 1.0 μg NO N m^{-2} h^{-1} (2.3 ± 0.09 kg NO N ha^{-1} yr^{-1}) and 31.1 ± 1.6 μg NO N m^{-2} h^{-1} (2.7 ± 0.1 kg NO N ha^{-1} yr^{-1}), respectively. The mean annual NO emission rate for the entire observation period 1995–1996 was 28.4 ± 0.9 μg NO N m^{-2} h^{-1} (2.5 ± 0.08 kg NO N ha^{-1} yr^{-1}). This emission rate was 3.2 and 1.9 times lower ($p < 0.001$) compared to the mean annual NO emission rate calculated for the spruce control site and the limed spruce site, respectively (Table 2).

In contrast to mean annual NO emission, no pronounced differences in mean annual NO_2 deposition rates could be detected between the different experimental sites and the different years of observation (Table 2). Therefore neither liming nor forest type had a striking effect on the magnitude of the annual mean NO_2 deposition rate to the forest floor. The mean annual NO_2 flux rate calculated for the entire observation

Table 2. Mean Annual NO and NO_2 Flux Rates, Minimum and Maximum Mean Daily NO and NO_2 Flux Rates, Coefficient of Variation (CV), and Mean Annual Net NO_x Flux Rate at the Different Sites for 1994, 1995, and 1996

Experimental Site	1994	1995	1996	Mean 1994–1996
		NO		
Spruce, control				
Annual mean	72.7 ± 2.1	99.8 ± 3.1	103.5 ± 4.0	91.8 ± 1.9
Minimum/maximum	15.6/243.6	5.4/278.6	4.1/380.2	
N	357	341	350	
CV, %	55.2	56.9	71.7	65.6
Spruce, limed				
Annual mean	62.1 ± 2.6[a]	38.7 ± 1.0	40.3 ± 1.5	47.2 ± 1.1
Minimum/maximum	9.2/291.6	1.7/125.5	3.9/133.3	
N	357	342	351	
CV, %	78.5	46.9	71.1	76.5
Beech, control				
Annual mean	8.7 ± 0.3[b]	25.8 ± 1.0	31.1 ± 1.6	28.4 ± 0.9[c]
Minimum/maximum	1.5[b]/15.9[b]	3.0/115.3	4.9/158.5	
N	106	334	328	
CV, %	35.2[b]	70.6	93.0	85.2
		NO_2		
Spruce, control				
Annual mean	−27.0 ± 0.6	−32.9 ± 0.9	−29.8 ± 1.0	−29.9 ± 0.5
Minimum/maximum	−67.4/−6.82	−78.6/−4.3	−130.4/3.3	
N	357	337	348	
CV, %	44.1	49.0	63.4	53.7
Spruce, limed				
Annual mean	−31.6 ± 0.8[a]	−29.2 ± 0.7	−28.5 ± 0.8	−29.8 ± 0.5
Minimum/maximum	−72.5/−7.7	−75.2/0.2	−80.3/−3.0	
N	354	338	347	
CV, %	49.0	47.0	50.1	48.9
Beech, control				
Annual mean	−19.3 ± 0.9[b]	−22.7 ± 0.6	−26.2 ± 0.7	−24.4 ± 0.5[c]
Minimum/maximum	−42.4[b]/−4.1[b]	−82.3/−5.0	−63.3/−5.1	
N	106	331	327	
CV, %	45.7[b]	50.5	48.5	50.0[c]
		Net NO_x Flux		
Spruce, control	45.4 ± 2.0	66.6 ± 2.7	73.8 ± 3.9	61.7 ± 1.7
Spruce, limed	30.0 ± 2.1	9.6 ± 1.1	11.8 ± 1.8	17.3 ± 1.1
Beech	−10.7 ± 0.9[b]	3.2 ± 1.1	4.9 ± 1.7	4.0 ± 1.0[c]

Flux rates are in $\mu g\ N\ m^{-2}\ h^{-1}$. *N*, total number of observation days per year for which NO and NO_2 flux rates were obtained.

[a] Experimental site was limed on March 10, 1994.

[b] Measurements started on September 15, 1994.

[c] Only data from 1995 and 1996 were used for calculation.

period was approximately $-29.9 \pm 0.5\ \mu g\ NO_2\ N\ m^{-2}\ h^{-1}$ (2.6 ± 0.04 kg NO_2 N $ha^{-1}\ yr^{-1}$) for both the spruce control site and the limed spruce site and was $-24.4 \pm 0.5\ \mu g\ NO_2\ N\ m^{-2}\ h^{-1}$ (2.1 ± 0.04 kg NO_2 N $ha^{-1}\ yr^{-1}$) at the beech site (Table 2).

Since annual NO emission generally exceeded annual NO_2 deposition (Table 2), a net annual NO_x emission resulted at all experimental sites from the soil (Table 2). The mean annual net NO_x emission calculated for the entire observation period 1994–1996 at the spruce control site and the limed spruce site amounted to $61.7 \pm 1.7\ \mu g\ NO_x\ N\ m^{-2}\ h^{-1}$ (5.4 ± 0.2 kg NO_x N $ha^{-1}\ yr^{-1}$) and $17.3 \pm 1.1\ \mu g\ NO_x\ N\ m^{-2}\ h^{-1}$ (1.5 ± 0.1 kg NO_x N $ha^{-1}\ yr^{-1}$), respectively. At the beech site (1995–1996) this value was $4.0 \pm 1.0\ \mu g\ NO_x\ N\ m^{-2}\ h^{-1}$ (0.4 ± 0.1 kg NO_x N $ha^{-1}\ yr^{-1}$). Therefore the soil of the spruce control site was an ~4 times stronger source for NO_x than the soil of the limed spruce site and was an ~15 times stronger source for NO_x than the soil of the beech site (Table 2).

A comparison of annual coefficients of variation of NO fluxes (Table 2) shows highest coefficient of variation (CV) values for 1996 reflecting the enormous temporal and seasonal fluctuations of NO emission rates during spring, summer, and autumn (see also Figures 1 and 3). The relative high CV value for NO emission rates of the limed spruce site in 1994 reflects the effect of liming on NO emission, which was becoming obvious from September until the end of 1994. CV values for NO_2 flux rates did not change markedly over the years and for the experimental sites (~50%) except for the spruce control site in 1996 (CV value ~63%), reflecting the enormous temporal variations in NO_2 deposition rates occurring during May 1996 (Figure 2).

3.3. Identification of Soil Layers and Microbial Processes Most Important for NO Emission

In the experiments performed with intact soil cores taken from the different experimental sites we found that the organic layer of the spruce control site contributed >86% to the actual NO emission from the soil into the atmosphere, whereas deeper soil layers contributed significantly less (<14%). For the limed spruce site we found that the organic layer and deeper soil layers contributed ~79% and 21%, respectively, to the actual NO emission (Table 3). However, differences between sites were not significantly different ($p > 0.05$). For the beech site data are not available. Gaseous inhibitor studies on intact soil cores taken from the different experimental sites at different seasons during 1994–1996 in order to differentiate between the contribution of nitrification and denitrification to the actual NO emission revealed that regardless of the site studied, the mean contribution of nitrification and denitrification to the actual NO emission was ~65% and 35%, respectively (Table 4). It is noteworthy that the relative contribution of nitrification and denitrification to NO emission remained unchanged even on the limed spruce site, though in the organic layer of this site there was (1) a 61% increase in net nitrification rates and (2) a dramatic increase in cell numbers of microbial populations known to be involved in NO production/consumption (heterotrophic nitrifiers, autotrophic ammonia, and nitrite oxidizers and denitrifiers) as compared to the untreated spruce control site [*Papen and Butterbach-Bahl*, this issue].

3.4. Apparent NO and NO_2 Compensation Concentrations of Soils

We used individual NO and NO_2 flux rates and simultaneously measured NO and NO_2 concentrations at the outlet of measuring chambers to clarify whether for defined time periods showing constant environmental conditions (temperature, soil moisture), (1) apparent NO and NO_2 compensation concentrations could be demonstrated to exist for the soil of the different sites and (2) liming or forest type lead to changes in magnitude of NO and NO_2 compensation concentrations. Apparent compensation concentrations were only found for NO for soils of the spruce control and limed spruce site. Figure 5 gives results obtained from two individual dynamic chambers, which are representative for the mean apparent compensation concentration calculated for the soil of the spruce control site and the limed spruce site of the entire observation period. In the example given, for the soil of the spruce control site the apparent NO compensation concentration was 71.8 ppbv, whereas it was 36.4 ppbv for the soil of the limed spruce site, indicating that liming resulted in a marked decrease of the apparent NO compensation concentration. A more rigorous analysis of all data obtained for different dynamic chambers at different seasons for the spruce control and limed sites (Table

Table 3. Contribution of the Organic Layer and of the Mineral Soil at the Spruce Control Site and the Spruce Limed Site to the Actual NO Flux Rate Into the Atmosphere

	Spruce, Control, μg NO N m^{-2} h^{-1}	Spruce, Limed, μg NO N m^{-2} h^{-1}
Control, i.e., without removal of the organic layer	132.5 ± 22.1	47.0 ± 3.2
Organic layer removed	18.4 ± 0.6	9.9 ± 5.0
Change of NO emission rates compared to the control, %	−86.1[a]	−78.9[a]

Values represent means and standard error of flux rates obtained from laboratory studies on intact soil cores taken at the Höglwald experimental sites in May 1995 ($n = 2$).

[a] Not significantly different at level $p < 0.05$.

Table 4. Mean Contribution (September 1994 to May 1996) of Nitrification and Denitrification to Total NO Emission at the Different Experimental Sites of the Höglwald Forest as Calculated From Monthly Performed Inhibitor Studies on Intact Soil Cores

	Nitrification, %	Denitrification, %	*N*
Spruce, control	64.2 ± 3.7 (a)	35.8 ± 5.7 (b)	24
Spruce, limed	66.2 ± 4.4 (a)	33.4 ± 5.7 (b)	24
Beech	64.8 ± 4.4 (a)	35.2 ± 4.5 (b)	24

Different indices (a, b) indicate significant differences in contribution at the 95% confidence level. No significant differences were detected between the different experimental sites.

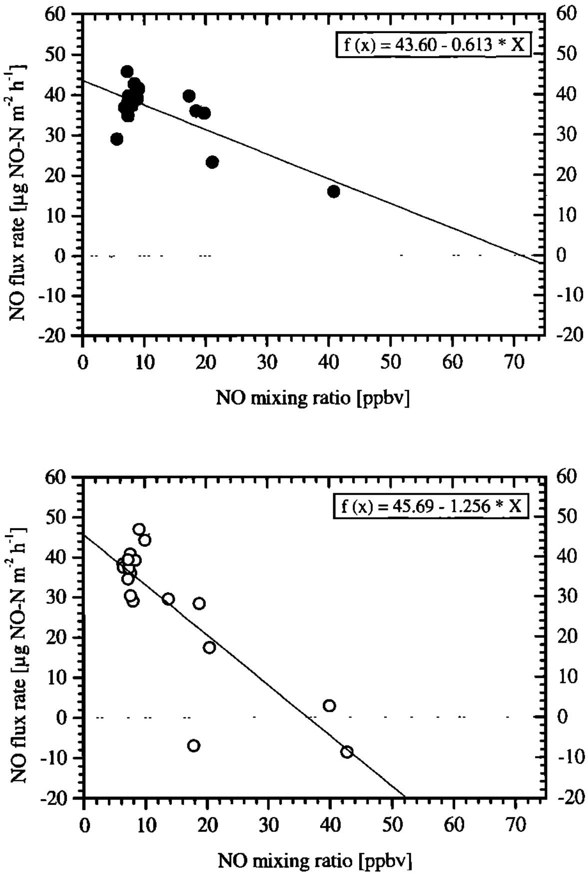

Figure 5. Representative examples for determination of apparent in situ NO compensation points of the soil of the spruce control site (solid circles) and the limed spruce site (open circles). In situ NO flux rates obtained from an individual dynamic chamber installed at the spruce control site and the limed spruce site were plotted against the simultaneously measured in situ NO mixing ratio at the outlet of the respective dynamic chamber. The intercept of the regression line with the abscissa gives the apparent NO compensation point, at which net NO flux between the soil and the atmosphere is zero. The apparent NO compensation points of the soil of the spruce control site and the limed spruce site were 71.8 and 36.4 ppbv, respectively. The gross NO production rates, given by the intercept of the regression line with the *Y* axis, were 43.6 μg NO N m^{-2} h^{-1} for the soil of the spruce control site and 45.7 μg NO N m^{-2} h^{-1} for the soil of the limed spruce site. Examples given are for the time period November 7–8, 1994.

Table 5. Mean Gross NO Production Rates P, NO Uptake Rate Constants k, and Apparent NO Compensation Points m_c Obtained for Different Observation Periods

	Spruce, Control			Spruce, Limed		
	P	k	m_c	P	k	m_c
Date						
Oct. 12–14, 1994	68.0 ± 9.9	1719 ± 60	63.3 ± 8.9	38.0 ± 5.4	1235 ± 157	49.2 ± 0.7
Nov. 7–8, 1994	55.3 ± 11.3	936 ± 11	94.6 ± 19.3	29.7 ± 8.0	1511 ± 210	30.4 ± 6.8
Oct. 10–12, 1995	59.8 ± 17.0	1219 ± 112	86.5 ± 34.4	63.7 ± 19.8	1844 ± 258	50.9 ± 12.0
Dec. 8–10, 1995	25.1 ± 2.8	1024 ± 90	41.3 ± 9.1	41.6 ± 20.3	1740 ± 342	37.0 ± 13.2
Jan. 12–14, 1996	37.5 ± 8.4	1029 ± 61	57.6 ± 9.7	45.0 ± n.d.	1416 ± n.d.	50.8 ± n.d.
Mean	50.4 ± 6.0[a]	1203 ± 78[b]	69.9 ± 9.6[b]	45.1 ± 8.5[a]	1638 ± 135[b]	41.8 ± 5.5[b]
N	18	18	18	17	17	17

In addition, the mean for the entire observation period is given. P, NO gross production rate, μg NO N m^{-2} h^{-1}; k, NO uptake rate constant, L m^{-2} h^{-1}; m_c, apparent NO compensation concentration, ppbv; n.d., no statistical tests could be performed ($N = 1$), N, total number of cases, for which apparent NO compensation concentrations could be demonstrated to exist.

[a] Not significantly different at level $p < 0.05$.

[b] Significantly different at level $p < 0.01$.

5) revealed that integrated over 1994–1996, there was a significant ($p < 0.05$) reduction by 40% in the mean apparent NO compensation point of the soil of the limed spruce site (41.8 ± 5.5 ppbv) as compared to the soil of the spruce control site (69.9 ± 9.6 ppbv). This means that the soil of the limed spruce site did function as a net sink for atmospheric NO at 1.7 times lower ambient NO mixing ratios than the soil of the spruce control site. The reduction in NO emission could be due either to stimulation of NO consumption processes or to reduction of NO production within the soil. Table 5 shows that liming had not led to a significant decrease of the mean gross NO production rate (see also Figure 5, intercept of the regression lines with the Y axis) but did lead to a highly significant increase of the mean value of the NO uptake rate constant (k) (given by the slope of the regression line in Figure 5; k in Table 5) by 36%, indicating that the reduction of NO emission from the soil of the limed spruce site was due to stimulation of NO consumption.

3.5. Correlation of NO and NO_2 Flux Rates With Nonbiotic and Biotic Parameters

The results obtained from multiple regression analysis between NO and NO_2 flux rates and the parameters soil temperature (organic layer), soil moisture (% WFPS), and NH_4^+ and NO_3^- concentrations are presented in Table 6. Obviously, the sequence of importance of the different parameters tested on NO emission rates was soil temperature to % WFPS to NO_3^- concentration to NH_4^+ concentration. Only for the limed spruce site were the parameters % WFPS and soil NO_3^- concentrations of comparable importance on NO emission rates (Table 6). With regard to NO_2 flux rates, coefficients of determination were extremely low, indicating that none of the parameters tested had a strong influence on NO_2 deposition rates. It is also noteworthy that for NO emission rates, coefficients of determination could explain variations of NO flux rates at the untreated sites at best by 39.1% and at the limed spruce site by 48.9% (Table 6).

In view of these results, regression analyses were performed in which only soil temperature and % WFPS were considered as the dominating modulators of NO emission (Tables 7 and 8). At least for soil temperature it was more adequate to use an exponential rather linear regression model. It is clear from Table 7 that at the spruce sites best correlations between NO emission rates and soil temperature were found at values of WFPS <45% and at the beech site at values of 55–65%. Coefficients of determination indicate that 76.6% (spruce control site), 71.1% (limed spruce site), and 39.2% (beech site) of

Table 6. Results of Multiple Regression Analysis Between NO and NO_2 Flux Rates and the Soil Temperature, WFPS, and Soil NO_3^- and NH_4^+ Concentrations of the Organic Layer at the Experimental Sites of the Höglwald Forest

	Total r^2	Temperature r^2	WFPS r^2	NO_3^- r^2	NH_4^+ r^2
		NO Flux Rate			
Spruce, control	0.391[c]	0.300[c]	0.023[c]	0.017[b]	0.005[a]
Spruce, limed	0.489[c]	0.250[c]	0.163[c]	0.165[c]	0.005[b]
Beech	0.359[c]	0.299[c]	0.135[c]	0.049[c]	n.s.
		NO_2 Flux Rate			
Spruce, control	0.011[b]	0.011[b]	n.s.	n.s.	n.s.
Spruce, limed	0.046[c]	n.s.	n.s.	0.046[c]	n.s.
Beech	0.013[b]	0.013[b]	n.s.	n.s.	n.s.

Total r^2 represents the coefficient of determination when all parameters tested were included; otherwise, r^2 is calculated from standardized regression coefficient. Correlation is positive; n.s., not significant.

[a] Significant at level $p < 0.05$.

[b] Significant at level $p < 0.01$.

[c] Significant at level $p < 0.001$.

Table 7. Exponential Regression Analysis Between Soil Temperature and NO Flux Rates for Defined Ranges of Water-Filled Pore Space

	Spruce, Control				Spruce, Limed				Beech			
	r^2	p	N	Q_{10}	r^2	p	N	Q_{10}	r^2	p	N	Q_{10}
Water-filled pore space, %												
<45	0.766	a	76	2.90	0.710	a	76	2.89		n.c.		
>45–<55	0.541	a	172	2.80	0.522	a	172	2.28	0.264	a	120	2.25
>55–<65	0.482	a	303	3.11	0.493	a	303	2.80	0.392	a	95	2.70
>65	0.406	a	264	2.76	0.318	a	264	2.23	0.358	a	304	3.54
Mean				2.89				2.55				2.83

Q_{10} values were calculated for the temperature increase from 5°C to 15°C. For analysis, data of soil moisture and of soil temperature in the organic layer (spruce sites) and in 5 cm soil depth (beech site) were used. r^2, coefficient of determination; correlation is positive for r^2; n.c., no cases; N, number of cases.

[a]Significant at level $p < 0.001$.

variations in NO emission rates could be explained by variations in soil temperature. Mean Q_{10} values for the different sites calculated for the temperature increase from 5°C to 15°C were in a range between 2.55 and 2.89 but were not significantly different (Table 7). Correlation analysis between NO emission rates and % WFPS for different temperature ranges revealed that at all sites, best correlations were found in a temperature range 6–10°C and, additionally, for the spruce control and beech site, at temperatures >14°C (Table 8). However, coefficients of determination were markedly stronger for the limed spruce and beech site as compared to the spruce control site (Table 8).

Correlation analysis between NO emission rates and additional abiotic and biotic factors revealed the following sequence of importance for the spruce control and beech site: net nitrification rate to NH_4^+ input by wet deposition to NO_3^- input by wet deposition to sum of precipitation. For only the limed spruce site, NH_4^+ and NO_3^- input by wet deposition was of comparable importance in modulating NO emission (Table 9). At the spruce control site and beech site, ~65% and at the limed spruce site ~60% of variations of NO emission rates could be explained by variations of net nitrification rates, indicating that at all sites, nitrification was a key process for the in situ NO emission observed (Table 9). Regarding NO_2, NO_3^- input by wet deposition had a stronger impact on NO_2 deposition rates than NH_4^+ input at the spruce control and limed spruce site, whereas the other parameters tested had no significant effect on NO_2 deposition. At the beech site, none of the tested parameters had any significant influence on NO_2 deposition (Table 9).

3.6. Amount of N Input by Wet Deposition Lost From the Soil in Form of NO N

Our results show that at the N-saturated Höglwald Forest, there is a significant linear relationship between the amount of in situ N input by wet deposition and the magnitude of in situ NO emission rates from the soils (Table 9 and Figure 6). Since the amount of N input by dry deposition was not determined in our study, its direct impact on magnitude of NO and NO_2 fluxes could not be evaluated. However, since most of dry deposition will occur within the canopy but will partly be washed down to the soil via throughfall, part of the effect of dry deposition on magnitude of NO and NO_2 flux rates is included in the correlation analysis between NO and NO_2 flux rates and amount of in situ N input by wet deposition. Furthermore, since N input by wet deposition was determined only at weekly intervals, our data set does not indicate if there was a time lag between actual N input by wet deposition and the change in magnitude of NO and NO_2 fluxes.

From the slopes of the regression lines given in Figure 6 the fraction of N input that was released again from the soil in the form of NO can be calculated. At the spruce control site and limed spruce site, N input by wet deposition amounts to 30 kg N ha^{-1} yr^{-1}, whereas it is 20 kg N ha^{-1} yr^{-1} at the beech site [*Kreutzer*, 1995; *Rothe*, 1997]. The fraction of N lost (from the amount of N input by wet deposition) in form of NO N

Table 8. Dependency of NO Flux Rates on Changes in WFPS

Organic Layer Temperature, °C	Spruce, Control			Spruce, Limed			Beech		
	r^2	p	N	r^2	p	N	r^2	p	N
>2–<6		n.s.		0.177	c	197	0.092	b	114
>6–<10	0.074	c	196	0.392	c	196	0.356	c	114
>10–<14	(0.024)	a	160	0.046	b	160	0.172	c	126
>14	0.065	b	84		n.s.		0.385	c	48

The 1994–1996 data set with daily resolution was classified for different temperature ranges before a linear regression between WFPS and NO flux rates was performed. Correlation is positive for r^2; except value in parentheses which has a negative correlation; n.s., not significant; N, number of cases.

[a]Significant at level $p < 0.05$.

[b]Significant at level $p < 0.01$.

[c]Significant at level $p < 0.001$.

Table 9. Results of Correlation Analysis Between NO Emission Rates and NO_2 Deposition Rates and NH_4^+ and NO_3^- Input by Wet Deposition, Sum of Precipitation (Throughfall), and Net Nitrification Rates for the Spruce Control Site, the Limed Spruce Site and the Beech Site at the Höglwald Forest

	NO Emission Rate			NO_2 Deposition Rate		
Parameter	Spruce, Control r^2	Spruce, Limed r^2	Beech r^2	Spruce, Control r^2	Spruce, Limed r^2	Beech r^2
NH_4^+ input by wet deposition	0.600[b]	0.220[b]	0.340[b]	0.120[a]	0.270[b]	n.s.
N	32	32	37	31	32	
NO_3^- input by wet deposition	0.480[b]	0.250[b]	0.270[b]	0.240[b]	0.370[b]	n.s.
N	32	32	37	32	32	
Sum of precipitation (throughfall)	0.130[a]	n.s.	0.240[b]	n.s.	n.s.	n.s.
N	32		36			
Net nitrification rate in the organic layer	0.653[b]	0.604[b]	0.648[b]	n.s.	n.s.	n.s.
N	21	20	21			

Correlation analyses were performed using weekly data, except for correlation analysis between net nitrification rates and NO emission and NO_2 deposition rates, for which monthly data were used. Correlation is positive for r^2; n.s., not significant; *N*, number of cases.

[a] Significant at level $p < 0.05$.

[b] Significant at level $p < 0.01$.

amounted to 15% (4.6 kg NO N ha^{-1} yr^{-1}) at both spruce sites, whereas it was 7% (1.4 kg NO N ha^{-1} yr^{-1}) at the beech site. This result shows that there is an impact of forest type on the fraction of N input which is lost from the soil in form of NO, at least under conditions of N saturation. In addition, the "background" NO emissions (i.e., at zero N input by wet deposition) from the N-saturated sites were 72 g NO N ha^{-1} $week^{-1}$ (3.8 kg NO N ha^{-1} yr^{-1}) at the spruce control site and 27 g NO N ha^{-1} $week^{-1}$ (1.4 kg NO N ha^{-1} yr^{-1}) at the beech site (as derived from the intercepts of the regression lines with the *Y* axis in Figure 6).

4. Discussion

4.1. NO and NO_2 Flux Rates at the Höglwald Forest as Compared to Other Studies of Temperate Forests

Table 10 is a compilation of ranges of NO and NO_2 flux rates reported by different authors for different temperate coniferous and deciduous forest ecosystems including the results obtained from our study. As far as mean NO flux rates were given in the literature, the long-term annual mean NO emission rate from the soil of the spruce control site of the Höglwald Forest was between 3.1-fold and 153-fold higher than mean NO emission rates reported by others from temperate coniferous forest ecosystems. Mean NO emission rates from soil of the beech site were onefold to 142-fold higher than mean NO emission rates reported for other temperate deciduous forests (Table 10). If we compare the mean NO emission rate at the spruce control site (91.8 μg NO N m^{-2} h^{-1}) obtained from our continuous measurements with the mean rate (26.3 μg NO N m^{-2} h^{-1}) calculated from short-term measuring campaigns performed during an earlier study (1990–1992) at the Höglwald Forest [*Papke and Papen*, 1998], this earlier work underestimated NO flux almost fourfold (Table 10), demonstrating the need of long-term continuous measurements with high temporal resolution, in order to estimate the annual soil NO source strength more reliably. Though we observed a decrease in NO emission rates by 49% after liming of one of the spruce sites, emission rates remained 1.6-fold to 78.7-fold higher as compared to NO flux rates for other temperate coniferous forests (Table 10).

In contrast to most other studies (Table 10) we determined simultaneously both NO emission and NO_2 deposition rates (Figures 1–4). Therefore we were able to calculate net NO_x emissions, which showed extreme differences in magnitude between the coniferous and deciduous site (Table 2 and Figures 1–4). It is noteworthy that NO_2 deposition rates at the Höglwald site were markedly higher than reported for other temperate forest ecosystems (Table 10). We assume that the extremely high NO emission and NO_2 deposition rates observed at the Höglwald Forest as compared to other temperate forests are the consequence of both N saturation [*Kreutzer*, 1995; *Rennenberg et al.*, 1998] as well as chronically high loads of atmospheric N input. It has been stressed by, e.g., *Aber et al.* [1989] that increasing atmospheric N deposition will lead to N saturation of temperate forest ecosystems, enhanced mineralization, and nitrification rates and, in consequence, to enhanced NO_3^- leaching into the groundwater and increasing release of N trace gases from forest soils. Recently, it has been pointed out by *Fenn et al.* [1996] that the magnitude of NO emission from forest soils may be indicative for both the de-

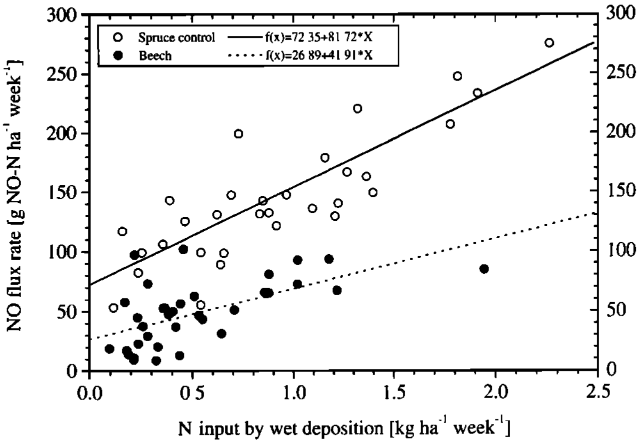

Figure 6. Linear regression analysis between weekly mean NO emission rates and weekly amounts of N input (sum of NH_4^+ and NO_3^-) by wet deposition (measured in the throughfall [*Huber*, 1997]) at the spruce control and the beech site of the Höglwald Forest (data obtained in the time period January 1, 1994, to December 31, 1994 (spruce sites), and September 15, 1994, to June 30, 1995 (beech site), respectively, were used for correlation analysis).

gree of N saturation of forest ecosystems as well as the degree of atmospheric N deposition to which forests are exposed. Our results (see also section 4.5) strongly support these hypotheses/suggestions.

4.2. Liming of Forest Soil and Its Impact on NO, NO_2 Flux Rates, and NO and NO_2 Compensation Points

In this paper we have shown that when integrated over the entire observation period, surface application of lime to the soil of the spruce site resulted in significant reduction of NO emissions by 49%. This result is in accordance with findings by *Papen et al.* [1993] and *Papke and Papen* [1998], who, in an earlier study at the Höglwald Forest (1990–1992) performing short-term measuring campaigns at different seasons, found reductions in NO emissions between 43% and 100% from soil of a limed spruce site as compared to an unlimed spruce site. However, in this earlier study the soil of the limed spruce site did function as a net sink for atmospheric NO (Table 10), while in the present study the soil of the limed spruce site remained a source of NO during the entire observation period. This difference is most likely related to the fact that different stages of the effect of liming on NO emission were captured. The earlier study was performed 6–7 years after lime had been applied to the forest soil (long-term effects of liming), whereas our measurements represent the initial and short-term effects of lime application on NO emission.

The observed reduction in NO emission is in contrast to N_2O emission rates, which at the same sites did increase over the observation years by factors between 1.4 and 1.7 as compared to the untreated spruce control site [*Papen and Butterbach-Bahl*, this issue]. Obviously, liming did exert different effects on the magnitude of N trace gas species emitted from the soil. Since in the limed soil in the uppermost organic layer there was a significant increase in soil pH, an increase in net nitrification rates by 61%, and a dramatic increase in cell numbers of microbial populations capable of N trace gas production [*Papen and Butterbach-Bahl*, this issue], we would have expected an increase in NO emission from the soil, as was observed for N_2O [*Papen and Butterbach-Bahl*, this issue]. The finding that N_2O emission was enhanced but NO emission was reduced could theoretically be explained, for example, by a stimulation of NO consumption via denitrification. However, our results are not in accordance with such an explanation because the relative contribution of nitrification and denitrification for both NO emission and N_2O emission [*Papen and Butterbach-Bahl*, this issue] remained unchanged after liming (Table 4). This means that rates of NO and N_2O production via nitrification and denitrification must have been stimulated to the same extent at the limed site. Therefore we conclude from our results that at the limed site (1) the ratio of NO/N_2O produced during nitrification and (2) the ratio of NO/N_2O produced during denitrification were shifted in favor of N_2O.

The results obtained from our studies on apparent NO compensation concentrations, gross NO production, and the NO uptake rate constant strongly indicate that the reduction of NO emission was due to stimulation of NO consumption processes rather than to a decrease of gross NO production within the soil (Table 5). Since enhanced NO consumption did obviously not result in an equivalent increase in N_2O emission (and in view of the finding that nitrification and not denitrification was the main process for both NO and N_2O emission), we hypothesize that stimulation of oxidative rather than reductive NO consumption processes was responsible for the increased NO consumption in the soil of the limed spruce site. Such processes have unequivocally been demonstrated to exist in oxic soils and are catalyzed by both heterotrophic microorganisms [*Baumgärtner et al.*, 1996; *Koschorreck et al.*, 1996; *Rudolph et al.*, 1996; *Dunfield and Knowles*, 1997, 1998] as well as autotrophic nitrite oxidizers [*Freitag and Bock*, 1990]. It has been demonstrated that NO consumption by these processes did lead to NO_3^- production as the detectable end product and that N_2O was not produced by these processes [*Koschorreck et al.*, 1996; *Rudolph et al.*, 1996; *Dunfield and Knowles*, 1997]. We have detected a dramatic increase of cell numbers of autotrophic nitrite oxidizers by more than 3 orders of magnitude in the soil of the limed spruce site as compared to the soil of the control spruce site [*Papen and Butterbach-Bahl*, this issue]. At present, we can only speculate if these microorganisms and/or heterotrophic nitrifiers, the cell numbers of which also had significantly increased in the limed soil [*Papen and Butterbach-Bahl*, this issue], were responsible for the enhanced NO consumption in the limed soil.

The existence of NO compensation concentrations is a widespread phenomenon and was observed under both field and laboratory conditions [e.g., *Slemr and Seiler*, 1984; *Johansson and Granat*, 1984; *Remde et al.*, 1989; *Slemr and Seiler*, 1991]. We found in our study that liming had resulted in a significant reduction of the apparent (for discussion, see *Conrad* [1994]) NO compensation concentration from a value of 69.9 ppbv (spruce, control) to 41.8 ppbv (spruce, limed). This reduction was due to an increase in the NO uptake rate constant (k) rather than to a decrease of gross NO production rates (Table 5). Thus the soil of the limed spruce site had a pronounced higher affinity for NO uptake than the soil of the control spruce site, which is most likely the cause for the observed reduction of NO emission at the limed site. However, it must be stressed that NO concentrations in ambient air of >40 ppbv were rarely observed during the entire observation period at the Höglwald experimental site (mean value of NO concentration in ambient air was 2.8 ppbv). Thus the soil of both the control and the limed spruce sites did function predominantly as a net source for NO. NO compensation concentrations >75 ppbv (determined under field conditions and even higher as observed in this study) were also described by *Johansson and Granat* [1984] for fertilized agricultural soils in Sweden. We conclude that the high apparent NO compensation concentrations of the soil at the Höglwald site reflect the fact of high chronic N deposition from the atmosphere. This conclusion is in accordance with results obtained by *Slemr and Seiler* [1991], who also found higher NO compensation concentrations after N fertilizer application to a sandy loam soil in Germany as compared to an unfertilized soil.

In contrast to NO flux rates, no significant differences in annual mean NO_2 deposition rates were detected between the spruce control and the limed spruce site, indicating that microbial processes were not involved in NO_2 flux rates or, if involved, were not affected by liming. In the case of NO_2, chemical rather than microbial processes seem to modulate NO_2 flux [*Baumgärtner et al.*, 1992; *Skiba et al.*, 1997] from soils. In an earlier study at the Höglwald Forest [*Papke and Papen*, 1998] an influence of the (very sparse) ground vegetation on NO_2 flux rates could not be detected, indicating that NO_2 flux was predominantly determined by abiotic rather than biotic factors.

Table 10. Compilation of Published NO and NO_2 Flux Rates of Soils of Temperate Forest Ecosystems

Forest Type	NO_x Flux Rates, μg N m^{-2} h^{-1} NO	NO_x Flux Rates, μg N m^{-2} h^{-1} NO_2	Frequency of Chamber Measurements	Observation Period	Treatment	Reference
Coniferous						
Spruce, Höglwald (Germany)	10.5 to 55.2 (26.3)	−4.3 to −71.6 (−34.0)	six measuring campaigns, each lasting 2 weeks, 2-hour resolution	Dec. 1990 to March 1992	none	*Papke and Papen* [1998]
Spruce, Höglwald (Germany)	−14.2 to 8.6 (−2.8)	−15.8 to −44.8 (−30.0)	six measuring campaigns, each lasting 2 weeks, 2-hour resolution	Dec. 1990 to March 1992	6 years after 4 t dolomite ha^{-1} were applied	*Papke and Papen* [1998]
Spruce, Black Forest, Villingen (Germany)	0.2 to 1.3 (0.7)	−4.8 to −14.7 (−9.8)	eight measuring campaigns, each lasting 2 weeks, hourly resolution	May 1991 to Nov. 1993	none	*Hermann* [1996]
Spruce, Black Forest, Villingen (Germany)	−1.3 to 18.9 (10.1)	−3.9 to −31.5 (−17.7)	eight measuring campaigns, each lasting 2 weeks, hourly resolution	May 1991 to Nov. 1993	150 kg N ha^{-1} in form of $(NH_4)_2SO_4$ in May 1991	*Hermann* [1996]
Spruce, Black Forest, Schluchsee (Germany)	0.0 to 1.1 (0.6)	−1.5 to −3.5 (−2.5)	eight measuring campaigns, each lasting 2 weeks, hourly resolution	May 1991 to Nov. 1993	none	*Hermann* [1996]
Spruce, Black Forest, Schluchsee (Germany)	−0.7 to 3.6 (2.1)	−2.1 to −6.2 (−4.2)	eight measuring campaigns, each lasting 2 weeks, hourly resolution	May 1991 to Nov. 1993	150 kg N ha^{-1} in form of $(NH_4)_2SO_4$ in May 1991	*Hermann* [1996]
Spruce, Höglwald (Germany)	4.1 to 380.2 (91.8)	−3.3 to −130.4 (−29.9)	all year round continuous measurement for 3 years, hourly resolution, 120 flux rates per day for NO and NO_2	Jan. 1994 to Dec. 1996	none	this work
Spruce, Höglwald (Germany)	1.7 to 291.6 (47.2)	0.2 to −80.3 (−29.8)	all year round continuous measurement for 3 years, hourly resolution, 120 flux rates per day for NO and NO_2	Jan. 1994 to Dec. 1996	after 4 t dolomite ha^{-1} were applied on March 10, 1994	this work
Spruce (Scotland)	1.0 to 3.5	n.d.	daily or biweekly	. . .	none	*Skiba et al.* [1994]
Spruce, Pine, Sörentorp (Sweden)	0.4 to 2.7 (1.3)	n.d.	measurements for a few days with hourly to 2-hour resolution	June 1983	none	*Johansson* [1984]
Spruce, pine Sörentorp (Sweden)	0.4 to 21.6	n.d.	measurements for a few days with hourly to 2-hour resolution	June 1983	46.4 kg N ha^{-1} in form of $Ca(NO_3)_2$	*Johansson* [1984]
Pine, Jädraas (Sweden)	0.4 to 2.0 (0.8)	n.d.	measurements for a few days with hourly to 2-hour resolution	Aug.–Sept. 1983	none	*Johansson* [1984]
Pine, Jädraas (Sweden)	0.4 to 144	n.d.	measurements for a few days with hourly to 2-hour resolution	Aug.–Sept. 1983	46.4 kg N ha^{-1} in form of $Ca(NO_3)_2$	*Johansson* [1984]
Pine, Jädras (Sweden)	0.1 to 0.7	n.d.	measurements for a few hours on single days	June–July 1989	none	*Rondón et al.* [1993]
Pine, spruce, Simlangsdalen (Sweden)	0.3 to 1.4	n.d.	measurements for a few hours on single days	June–July 1990	none	*Rondón et al.* [1993]
Pine, forest in the northeastern German Lowland (Germany)	2.6 to 31.1 (12.1)	n.d.	two measuring campaigns, each lasting 3 weeks, hourly resolution	Aug. 1995, Nov. 1995	none	*Butterbach-Bahl et al.* [1997]
Mixed conifer forest, San Bernadino Mountains, California	(29.2)	n.d.	daily	August 9–16, 1993	dry soil	*Fenn et al.* [1996]
	(77.7)	n.d.	daily	August 9–16, 1993	wetting of soil	
Pine, spruce (birch)	0.0 to 138 (5.8)	n.d.	monthly	Sept. 1992 to Sept. 1994	peatland drained for forestry 40–50 years before measurements	*Lang et al.* [1995]

Deciduous						
Birch (Scotland)	0.004 to 6.1	n.d.	daily or biweekly	...	...	*Skiba et al.* [1994]
Alder (Scotland)	0.9 to 9.9	n.d.	daily or biweekly	...	...	*Skiba et al.* [1994]
Oak/hickory, Tennessee	0.2 to 4.0	(0.09)	daily or biweekly	Sept. and Oct. 1988	none	*Williams and Fehsenfeld* [1991]
Oak/hickory, Mississippi	(0.2)	n.d.	daily, 3-hour resolution	...	none	*Thornton and Valente* [1992]
Oak/hickory, North Carolina	(0.5)	n.d.	daily, 3-hour resolution	...	none	*Thornton and Valente* [1992]
Oak/hickory, Tennessee	(30.2)	n.d.	daily, 3-hour resolution	July 6–18, 1991	none	*Valente and Thornton* [1993]
Soil of cleared mixed coniferous-deciduous forest, Scotia, central Pennsylvania	0.64 to 14.8 (4.3)	(0.28)	daily	July 25–30, 1986	forest cleared in 1960s by removal of 45–60 cm of topsoil and vegetation	*Williams et al.* [1988]
Beech, Höglwald (Germany)	1.5 to 158.5 (28.4)	−4.1 to −82.3 (−24.4)	all year round continuous measurement for 2.3 years, hourly resolution, 120 flux rates per day for NO and NO_2	Sept. 1994 to Dec. 1996	none	this work

Positive rates, flux from the soil into the atmosphere (emission rates); negative rates, flux from the atmosphere into the soil (deposition rates); values in parentheses (so far given in the literature), mean flux rates; n.d., no data.

4.3. Soil Layers Most Important for NO Emission and Effect of Forest Type on NO and NO_2 Flux Rates

The most important soil layer for NO released into the atmosphere under spruce was identified to be the uppermost organic layer (Table 3), as was also found for N_2O at the Höglwald Forest [*Papen and Butterbach-Bahl*, this issue]. Our results obtained for the soil of the spruce sites are in accordance with results obtained by other authors, who also reported that the uppermost part of the soil was the most important layer for the actual NO released from soil into the atmosphere [*Johansson and Granat*, 1984; *Slemr and Seiler*, 1984; *Skiba et al.*, 1993].

In this study we have found that forest type obviously influences the magnitude of NO emission from soil. Annual mean NO emission rates from soil of the spruce control site were ~3 times higher than those from the soil grown with beech (Table 2). This could be due, for example, to lower NO production or higher NO consumption within the soil of the beech site as compared to the soil of the spruce control site. The results obtained for N_2O emission from the soil under beech showed that under beech deeper soil layers (Ah horizon) contributed to a higher degree to the observed N_2O emission than the organic layer [*Papen and Butterbach-Bahl*, this issue]. If this should also apply for NO emission at the beech site, the reduction in NO emission from soil under beech could be partly due to restricted NO diffusion both through the smaller pores of the mineral soil layer (Ah) as well as through the more dense material of the organic layer (broad leaves) at the beech site as compared to the spruce site. Thus owing to an enhanced residence time of the NO produced in the soil, NO had a higher probability to be consumed before it could escape into the atmosphere. However, the present database does not allow us to support or discard any of these hypotheses.

4.4. Abiotic and Biotic Parameters Modulating NO and NO_2 Flux Rates

Our results obtained from multiple regression analysis between NO emission and the parameters temperature and soil moisture have shown that both parameters significantly correlated with in situ NO emissions but that correlation with temperature was stronger than correlation with soil moisture. In accordance with results obtained by others [*Williams et al.*, 1988; *Shepherd et al.*, 1991; *Slemr and Seiler*, 1991; *Valente and Thornton*, 1993; *Kim et al.*, 1994; *Aneja et al.*, 1996; *Thornton et al.*, 1997; *Skiba et al.*, 1997], the relationship between soil temperature and NO emission was better described using an exponential rather than a linear regression model. In contrast to soil temperature the relationship between soil moisture (% WFPS) and NO emission rates was better described using a linear rather than an exponential regression model. We found that at the optimal temperature range between 6°C and 10°C, for which correlations were shown to be strongest (Table 8), the maximum of NO emission rates was found at <45% WFPS at the spruce and 55–65% WFPS at the beech site (Table 7). Our results are in good agreement with reports of others, who also found maximal NO emission rates at WFPS <60% [*Davidson*, 1991, 1993; *Riley and Vitousek*, 1995; *Cárdenas et al.*, 1993]. For the Höglwald Forest sites we have found Q_{10} values (5°C–15°C) for NO emission rates between 2.23 and 3.54. These values are in good agreement with Q_{10} values of NO emission reported by *Johansson and Granat* [1984], who found Q_{10} values (10°C–20°C) between 2.7 and 3.6 for agricultural soils in Sweden.

Among the other abiotic factors also included in the multiple regression analysis, soil NO_3^- and NH_4^+ concentrations were found to correlate positively with NO emission. However, coefficients of determination were markedly weaker as compared to soil temperature and soil moisture. Other authors have also reported positive correlations between NO emission and NH_4^+ and/or NO_3^- concentrations of soils [e.g., *Meixner et al.*, 1997; *Thornton and Valente*, 1992]. However, in another set of studies, either no correlation or only a weak positive correlation to concentrations of inorganic nitrogen in the soil was found [e.g., *Williams et al.*, 1992; *Lang et al.*, 1995]. These partly contradictory findings lead to the conclusion that soil pools of NH_4^+ and NO_3^- are of minor importance for the prediction of NO emission rates. Hence microbial N turnover rates (e.g., nitrification rates) rather than NH_4^+ and NO_3^- concentrations might be better indicators to follow. The results obtained in our study strongly support this assumption: the central role of nitrification for regulating the magnitude of NO emission from the soil of the Höglwald Forest could be demonstrated by the excellent positive correlation between rates of in situ net nitrification and in situ NO emission rates, which could explain >60% of the variation of NO flux rates at all sites studied (Table 9). The importance of nitrification for NO production and emission from different soils was also emphasized by other authors [e.g., *Remde and Conrad*, 1991; *Skiba et al.*, 1992, 1993; *Papen et al.*, 1993; *Hutchinson et al.*, 1993; *Neff et al.*, 1995; *Kester et al.*, 1997]. In most of these studies the importance of nitrification for the observed NO emission was identified by the use of inhibitors against autotrophic nitrification. Even in a study where net nitrification rates were determined in soil cores from a forested peatland, the database was not sufficient to detect a positive correlation between actual nitrification and NO emission rates [*Lang et al.*, 1995]. To our knowledge, we have demonstrated for the first time that a strong positive correlation does exist between in situ NO emission rates and in situ net nitrification rates.

4.5. Impact of in Situ N Input on in Situ NO and NO$_2$ Flux Rates

Correlation analysis between in situ N input by wet deposition and in situ NO emission rates revealed that at the spruce control site and beech site, 61% and 36%, respectively, of the variation of NO emission rates could be explained by variations in the amount of in situ N input by wet deposition (NH_4^+ plus NO_3^-). For the spruce control site and the beech site this correlation was stronger for NH_4^+ input than for NO_3^- input (Table 9), which can be taken as further indication that nitrification was the predominant source for NO emission. Since the correlation between NO emission rates and amount of precipitation was markedly weaker than for the parameters NH_4^+ and NO_3^- input (Table 9), we conclude that the excellent correlation between NO emission and N input by wet deposition was not primarily due to amount of precipitation but was indeed due to the NH_4^+ and NO_3^- concentrations within the throughfall precipitation. In earlier studies it was indirectly concluded from N fertilization experiments, in which atmospheric N input into forest ecosystems was simulated by artificial application of N-compounds onto the soil [e.g., *Johansson*, 1984; *Hermann*, 1996; *Rennenberg et al.*, 1998] or from comparison studies of different forest sites receiving different amounts of N deposition [*Fenn et al.*, 1996; *Butterbach-Bahl et al.*, 1998] that a strong impact of N input on magnitude of NO emission rates from forest soils might exist. Our studies at the Höglwald Forest sites unequivocally demonstrate the existence of this relationship.

Our results derived from correlation analysis about the N loss in form of NO N per kg N input by wet deposition (measured in the throughfall) show that >17% of the actual N input (in form of $NH_4^+ + NO_3^-$) was released again from the soil into the atmosphere at the spruce sites, whereas this figure was 7% for the beech site. Thus the NO N loss rate from N input by wet deposition from a coniferous forest, the spruce site, was >2 times higher than the loss rate at the deciduous site indicating that forest type strongly influences the magnitude of N loss from N input in form of NO. The loss rates reported here are the highest ever reported in the literature for forest soils. *Johansson* [1984] reported that 0.35% of N fertilizer applied to a pine forest soil in Sweden in form of $Ca(NO_3)_2$ was released into the atmosphere. Comparable loss rates as found in this study were described by *Shepherd et al.* [1991], who reported NO N loss of 11% from bare soil in Canada fertilized with 33 kg NH_4NO_3 mixed with 67 kg limestone filler. In other studies, loss rates of fertilizer N from agricultural soils as NO in a range between 0.003% and 3.25% were reported depending on soil type, fertilizer type applied, and fertilizer application rate (for a summary, see *Skiba et al.* [1997]).

In this study for the spruce sites we have found a positive relationship between NO_2 deposition rates to the soil and the amount of inorganic N input by wet deposition (Table 9). The correlation was more pronounced for NO_3^- input than for NH_4^+ input. There was no evidence for any biological process involved in NO_2 deposition. Therefore we hypothesize that the positive relation between NO_2 deposition and N input by wet deposition could be the indirect result of enhanced NO emission rates according to the following scheme: emitted NO reacted with O_3 in ambient air to NO_2 leading to enhanced NO_2 concentrations in ambient air and, in consequence, to enhanced NO_2 deposition rates onto the soil surface.

4.6. Contribution of N-Affected Temperate Coniferous and Deciduous Forests to the Global Soil Source for NO$_x$

We used our database to estimate the contribution of N-affected temperate forest ecosystems to the global source strength of soils for NO_x. We differentiate in this calculation between the contribution of N-affected coniferous and deciduous forest ecosystems. We assume in our calculation that from the 10^6 km^2 of N-affected temperate forests [*Davidson and Kingerlee*, 1997], 0.5×10^6 km^2 are stocked with coniferous and 0.5×10^6 km^2 with deciduous forests, respectively. The long-term annual mean NO_x emission from the coniferous site (spruce) at the Höglwald was 5.4 kg NO_x N ha^{-1} yr^{-1}, whereas it was only 0.4 kg NO_x N ha^{-1} yr^{-1} for the deciduous site (beech), though both forest types of the Höglwald Forest had experienced years of elevated N deposition and are characterized by N saturation. Assuming that these marked differences in magnitude of NO_x emission demonstrated to exist for the Höglwald Forest between coniferous and deciduous forest types also apply for other N-affected coniferous and deciduous forest types, the contribution of these forest soils to the global NO_x emission from soils would be 0.3 Tg NO_x N yr^{-1}, whereas the contribution of N-affected deciduous forests would be negligible (<0.02 Tg NO_x N yr^{-1}). Our estimate is in excellent agreement with the estimate of *Davidson and Kingerlee* [1997], who estimated the contribution of N-affected temperate forests to the global NO emission from soils to be 0.3 Tg N yr^{-1}. However, we hypothesize that the area of temperate forest ecosystems exhibiting symptoms of N saturation will increase in the future if atmospheric N input is not reduced, since it must be realized that even presently N-limited forests under chronically elevated N input will, on a long-term scale, eventually change into N-saturated ecosystems and thus increasing sources of NO_x. Therefore we expect that the contribution of N-affected temperate forests to the global soil NO_x source strength will most likely increase in future.

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